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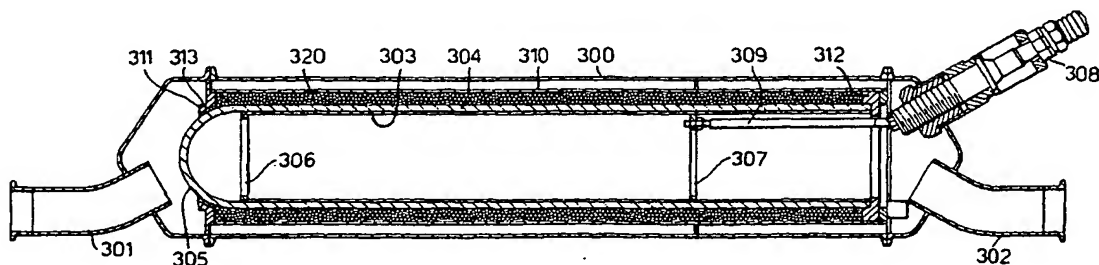
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(54) Title: REACTOR FOR PLASMA TREATMENT OF GASES



(57) Abstract: In a non-thermal plasma reactor (300), at least a component of the active material (320) is selected or modified to provide the capability to adsorb or trap a predetermined chemical species in the gas flow thereby to increase the effective residence time of said species relative to the residence time of unadsorbed species in the gas flow.

Reactor for Plasma Treatment of Gases

The invention relates to a reactor for plasma treatment of gases and more particularly to a method of  
5 manufacturing a reactor utilising a non-thermal plasma.

There is increasing interest in the use of non-thermal plasmas for treatment of gaseous exhausts and in particular for treatment of exhausts from motor vehicles.  
10 Treatment of exhausts involves conversion of harmful exhaust components such as hydrocarbons to carbon dioxide and water as well as harmful NO<sub>x</sub> components of exhausts to nitrogen. In the case of lean burn engines such as diesels there is a requirement for removal of  
15 carbonaceous particulates by for example oxidation to carbon dioxide. Examples of non-thermal treatment of exhausts are described in US 3,983,021 (Monsanto), US 5,147,516 (Tecogen) and US 5,254,231 (Battelle Memorial Institute). GB 2,274,412 (AEA Technology) describes a  
20 method for the treatment of diesel emissions by a non-thermal plasma for oxidation of carbonaceous particulates and reduction of NO<sub>x</sub> to nitrogen.

Plasma can be used to activate or produce reactant  
25 species, which then subsequently react with or without catalytic enhancement to yield the desirable products. For example, our publication WO99/12638 describes the plasma production of plasma activated hydrocarbons as a precursor to the selective catalytic reduction of NO<sub>x</sub> to  
30 N<sub>2</sub>. Examples of catalysts for this selective reduction of NO<sub>x</sub> to nitrogen are alkali metal-exchanged zeolite Y or silver aluminate. Other metal-exchanged or metal doped

zeolite material such as those known as Cu/ZSM-5, Fe/ZSM-5, Co/ZSM-5, zeolite beta and hydrogen exchanged zeolites such as H-ZSM-5 are suitable materials. Other suitable catalysts are aluminas including alpha, gamma, chi and other crystalline phases, oxides of titanium, zirconium, cerium and vanadium, perovskites, spinels and mixtures of these materials. Metal doped inorganic oxides such as cobalt-doped aluminas are also suitable materials. Examples of suitable catalysts are also described in an article 'Selective catalytic reduction of NO<sub>x</sub> with N-free reductants' by M Shelef published in Chem Rev 1995, pp209-225.

In such catalytically enhanced plasma processes the reactant species such as plasma activated hydrocarbons, which can include oxygenated hydrocarbons, are often produced as intermediates in e.g. the stepwise decomposition of hydrocarbons by reactions of O<sub>2</sub>, O, OH and HO<sub>2</sub>. Where the reactants are intermediates and the catalyst is highly selective to a given reductant, optimisation of the process can become difficult, if not impossible. This is because the completeness of the plasma reactions and hence the concentration of intermediates is controlled largely by the input power (joules per second) for a given residence time in the plasma reactor. This leads to the idea of a normalised unit expressed in joules per litre, which will determine the concentration of intermediates in a plasma reactor. For example in an article 'Plasma assisted catalytic reduction of NO<sub>x</sub> by BM Penetrante et al, SAE 982508, it is shown how the gas phase composition changes with input power expressed as joules per litre of gas volume for an exhaust flow in litres per unit time. This key parameter, joules/litre, is largely fixed by vehicle

constraints, i.e. reactor size, and the acceptable level of power input to the reactor in as far as all of the exhaust passes through the reactor.

5       The present invention is based upon an appreciation of the advantages that follow if one changes the residence time of selected species in the reactor, and thus breaks the, at present unavoidable, link between joules per litre input power and reactant species. This  
10 would lead to a simplification in the design and an improvement in the energy efficiency of plasma reactors.

      Examples have been given which show that, without catalytic enhancement, plasma reactors can produce  
15 quantities of undesirable by-products usually associated with partial oxidation of hydrocarbons (see 'Analysis of plasma-catalysis for diesel NO<sub>x</sub> remediation' by J Hoard and M L Balmer, SAE 982429), for example methyl nitrate, formaldehyde. A solution is offered if hydrocarbons can  
20 be retained for relatively long periods of time to achieve complete conversion to CO and CO<sub>2</sub>, while oxides of nitrogen may require a short residence time to avoid formation of acids.

25       It is an object of the present invention to provide a method of manufacturing a component for a non-thermal plasma reactor which addresses these problems.

      The invention provides, in one of its aspects, a  
30 method of manufacturing a component for a non-thermal plasma reactor for the treatment of gases, which method comprises assembling a bed of active material in an

enclosure having gas flow conduits for directing gas to flow through or over the bed of active material, providing electrodes adapted when electrically energised to generate non-thermal plasma in the gas, characterised  
5 in that at least a component of the active material is selected for its capability to adsorb or trap a predetermined chemical species in the gas flow thereby to increase the effective residence time of said species relative to the residence time of species in the gas flow  
10 which are not adsorbed or trapped.

Preferably the said active material or component thereof is selected for its capability to adsorb or trap a predetermined chemical species in the exhaust gas flow  
15 produced as a result of the combustion of fuel, and any modifier or additive therein, by the internal combustion engine.

Or further, the said active material or component  
20 thereof may be selected for its capability to adsorb or trap a predetermined chemical species in the gas flow produced by non-thermal plasma activation of constituents thereof.

25 In accordance with the invention in these circumstances the predetermined chemical species may be, but is not restricted to a species from the group comprising nitrogen, oxygen, oxides of nitrogen such as NO, NO<sub>2</sub>, oxides of carbon such as CO, CO<sub>2</sub>, water,  
30 hydrocarbons including saturated, unsaturated, cyclic, branched and un-branched hydrocarbons, oxygenated hydrocarbons such as aldehydes, ketones, alcohols, acids ethers and esters, aromatic hydrocarbons and derivatives thereof including poly aromatic hydrocarbon compounds,

oil fractions, fuel and partially burned fuel, air and  
air/fuel mixes, smoke, carbonaceous particulate including  
the soluble organic fraction and carbon, fine and  
ultrafine fraction, sulphur compounds including SO<sub>2</sub> and  
5 sulphates, organo-nitrogen species, acid gases,  
combustion modifiers/enhancers, additives such as urea,  
ammonia, cerium oxide (such as Eolys) and plasma  
activated species such as O, OH, O<sub>3</sub> activated  
hydrocarbons including partially oxygenated hydrocarbons/  
10 organic molecules and electronically and vibrationally  
excited state species.

The invention includes a non-thermal plasma reactor  
for the treatment of gases, comprising a bed of active  
15 material in an enclosure having gas flow conduits for  
directing gas to flow through or over the bed of active  
material, electrodes adapted when electrically energised  
to generate non-thermal plasma in the gas, characterised  
in that at least a component of the active material is  
20 modified so as to adsorb or trap a predetermined chemical  
species in the gas flow to increase the effective  
residence time of the said species relative to the  
residence time of species in the gas flow which are not  
adsorbed or trapped. The combination of packing material  
25 and the electrode spacing are chosen so as to generate  
the desired plasma conditions.

The function of the active material, or component  
thereof, having the capability to adsorb or trap selected  
30 species can be seen as that of a selective filter for  
that species.

In addition to the advantages, referred to above,

which result from the effective increase in residence time of the selected species, such a selective filter can operate to adsorb or trap the reactants and hold them for sufficient time for them to be activated by a plasma and/or selected filter to a state where they can react with for example  $\text{NO}_x$  to yield desirable products. In this role the filter material or trapped species in the presence of a plasma can be made to appear to act as a catalytic surface but importantly neither the plasma nor the selective filter nor the trapped species alone need have catalytic properties. One example of a trapped species is carbonaceous particulate material from a diesel engine, for example soot that consists mainly of elemental carbon. In the plasma region soot becomes exposed to plasma generated species for example oxygen atoms. Oxygen atoms or other plasma generated species may diffuse into, adsorb and react with soot. Other plasma generated species include but are not restricted to  $\text{OH}$ ,  $\text{O}_3$  and  $\text{NO}_2$ . For example it is known oxygen atoms can diffuse into soot and form aldehyde-type groups on the surface. Oxygenated soot has different activated and catalytic properties to non-oxygenated soot. In this example the surface of the reactant material, e.g. carbon is transformed into a catalyst.

25

A selective filter according to the present invention provides, by selective modification of residence times, a method of controlling and hence optimising the distribution of product species from a plasma reactor with a significant degree of independence from flow rate, reactor size or energy density. The method of controlling and hence optimising the distribution of product species may include a method for optimising the desorption of the selectively filtered

species or by-product from these species following material or plasma activation, for example by variation of the temperature or the filter material.

- 5           Following the selective filtration of carbonaceous particulate in the plasma region the operation of the selective filter according to the present invention also allows for the desorption and/or decomposition by reactive or thermal methods of the carbon functionalities
- 10   formed on the surface or in the bulk, such as for example aldehyde-type groups formed on the surface. However, an important aspect of this functioning of the selective filter is that it provides for the carbonaceous soot to be oxidised at low temperatures to  $\text{CO}_2$  and  $\text{CO}$ .
- 15   Ordinarily, carbonaceous soot combusts at high temperature in excess of  $500^\circ\text{C}$  whereas, utilising this function of the selective filter, the soot can be oxidised effectively at temperatures as low as  $100^\circ\text{C}$ . This is a major advance over prior art soot oxidation
- 20   catalysts where temperatures are typically lowered to  $250 - 300^\circ\text{C}$

A specific embodiment of the invention will now be described by way of example with reference to the

25   accompanying drawings, which illustrate one suitable form for the structure of a reactor and its bed of active material. In the drawings:

Figure 1 is a longitudinal section of the reactor,

30   and

Figure 2 is a schematic view showing the gas flow path through the reactor of Figure 1,

Referring to Figure 1, a reactor for the plasma



assisted processing of the exhaust emissions from internal combustion engines to remove noxious components therefrom consists of a reactor chamber 300 which has inlet and outlet stubs 301, 302, respectively, by means  
5 of which it can be incorporated into the exhaust system of an internal combustion engine.

Inside the reactor chamber 300 there is an inner electrode 303 which is supported within a dielectric tube  
10 304, made for example out of .-alumina which has its upstream end closed by a spherical dome 305 to facilitate the flow of exhaust gases through the reactor. The inner electrode 303 is supported in the dielectric tube 304 by two spider supports 306, 307. The inner surface of the  
15 dielectric tube can be metallised with a metal coating in order to increase the physical contact between the electrode and dielectric tube. The support 307 is connected to a high voltage input terminal 308 via a ceramic insulated feed 309 so that a potential of the  
20 order of kilovolts to tens of kilovolts and repetition frequencies in the range 50 to 5000 Hz can be applied to the inner electrode 303. Concentric with the inner electrode 303 and dielectric tube 304 is a grounded outer electrode 310 made for example of stainless steel. The  
25 dielectric tube 304 and outer electrode 310 are supported within the reactor chamber 300 by disks 311, 312 made of an insulating ceramic material, such as alumina. A compliant heat resistant material 313 is interposed between the electrode support 311 and the dielectric tube  
30 304.

The space between the dielectric tube 304 and the outer electrode 310 is filled with a bed of active material 320, shown in Figure 1, but omitted from Figure  
35 2 for clarity of representation of the gas flow paths.

As shown in Figure 2, the outer electrode 310 has a series of baffles 314 and slots 315 315a. The baffles 314 extend from the outer electrode 310 to the inner surface of the wall of the reactor chamber 300 and act as  
5 grounding connections as well as causing the exhaust gases to follow a convoluted path which has both axial, and circumferential components and being at least partially helical. There is also a radial component of flow, initially inwardly as the gas transfers from  
10 outside the outer electrode 310 to the space between the electrodes 310 and 303 and then outwardly as the gas returns to exit from outside the outer electrode 310. Thus there is also a spiral component in the flow.

15 The baffle 314 is arranged to divide the space between the electrode 310 and the reactor chamber 300 into six segments. At the gas inlet end three of these segments are closed off at 314a, 314b and 314c to axial gas flow and the remaining three segments are open to  
20 axial gas flow into the space between the electrode 310 and the reactor chamber 300. These latter three segments are closed off by the baffle 314 at the gas outlet end of the reactor. Consequently the gas is forced to pass via slot 315 radially into the space between the electrodes  
25 303 and 310 then passing in at least a partially helical manner before passing radially via the next slot 315a into the next segment of space between electrode 310 and reactor chamber 300. The baffle 314 leaves open this segment at the gas outlet end, allowing exhaust of the  
30 treated gas. Thus it will be seen that the exhaust gases both enter and leave the main part of the reactor 300 along the surface of the outer electrode 310 and the electrode supports 311, 312 have reliefs at their circumferences which are so positioned as to permit this  
35 to happen. Thus for a given gas velocity, the residence time of the exhaust gases in the electric field is

increased compared with either purely axial or radial flow. Note that in Figure 2 part of the electrode 310 has been shown cut away at 316. This cut away is shown in the Figure only to illustrate the flow of the exhaust gases  
5 as they pass between the electrodes 303 and 310 and does not represent a structural feature of the reactor.

For a reactor suitable for the present invention there may be adopted any other structural form as  
10 described in our patent specification WO99/12638, or in other embodiments described in the specification of our patent application PCT/GB 00/01881. The active material 320 comprises polymeric, ceramic, or metallic material which can be in the form of spheres, pellets, extrudates,  
15 fibres, sheets, coils, granules, wafers, meshes, frits, foams, honeycomb monolith or membrane in the plasma region of the non-thermal plasma. Combinations of one or more of the above can be used to create a structure with a non-uniform surface area and porosity, for example a  
20 graded porosity, when presented to the gas. Foams and monoliths can be ceramic, metallic or polymeric and examples of foams and monoliths include but are not limited to alumina, zirconia, titania, zeolite for foams and cordierite, silicon carbide, alumina, zeolite and  
25 FeCrAlloy for a honeycomb monolith reactor. The active material can also be a carbon combustion catalyst for example cerium oxide, alkali metal oxide, or lanthanum oxide/alkali metal oxide/vanadium pentoxide, vanadates such as metavanadates and pyrovanadates. At least a  
30 component of the active material 320 is selected or modified in order to adsorb or trap a predetermined chemical species in the gas flow thereby to increase the effective residence time in the reactor of the said species relative to the residence time of unadsorbed or  
35 untrapped species in the gas flow. The active material 320 may comprise a plurality of components each of which

adsorbs or traps a different chemical species thereby to increase the effective residence time in the reactor of each of the different adsorbed or trapped chemical species. It will be appreciated that a selected or  
5 modified component of the active material may adsorb or trap more than one selected chemical species. Also, where a plurality of components is provided each of which adsorbs or traps a different chemical species, the respective adsorptions may be different for each  
10 different adsorbed or trapped species, thus providing a correspondingly different increase in the effective residence time of each of the different adsorbed or trapped species.

15         Suitable non-thermal plasma reactors are those of the ferroelectric bed type comprising a bed of material contained between two electrodes, dielectric barrier or silent discharge type, pulsed corona discharge reactor or surface discharge reactor or combination of reactors.

20

When a gas molecule, for example, hydrocarbon enters a non-thermal plasma it resides in the plasma zone for a given period of time known as the residence time whereupon chemical reactions can occur. When a selective  
25 filter in accordance with the present invention is present in the plasma region the residence time of selected gas molecules in the plasma region increases. This is because a selected gas molecule on entering the plasma zone is adsorbed or trapped onto the surface of  
30 material in the bed, and can then be activated, react and desorb at a later time from the surface. The molecule now in the gas phase can readsorb onto different regions of the bed. This process of adsorption or trapping, activation or reaction, desorption and readsorption can

occur throughout the plasma region thus increasing residence times of selected molecules entering the plasma region allowing chemical reactions to occur more extensively. Controlled adsorption and desorption may be  
5 used as an overall strategy to control the gas mixture exiting the reactor. In another example the selective filter may adsorb or trap species prior to plasma activation and/or surface decomposition and subsequent desorption. The material composition, e.g. acidity  
10 (Bronsted and Lewis acid sites), pore size, pore shape, pore size distribution, surface area are characteristics which can be modified to effect different residence times and selectivity.

15 The method of the invention is further illustrated by considering the specific example of removing carbonaceous particulate in the form of soot.

Attention has been focussed in most prior art  
20 arrangements on the removal of nitrogen oxides, without consideration of soot removal, typically by passing the gases containing the nitrogen oxides and soot for treatment through a non-thermal plasma reactor which contains no packing material (unpacked reactor), followed  
25 by a suitable selective reduction catalyst. The role of the plasma is to convert NO to NO<sub>2</sub> via a peroxy oxidation chain mechanism. The initial steps of this mechanism are believed to be dependant upon the reaction of O atoms, formed by the plasma, with hydrocarbons which through a  
30 chain mechanism (involving O<sub>2</sub> and OH reactions with the hydrocarbons and products of the O and hydrocarbon reactions) form peroxy species which are implicated in the NO to NO<sub>2</sub> oxidation reaction. The NO<sub>2</sub> in the presence of hydrocarbons in the exhaust gas is reduced to nitrogen

by the catalyst by a hydrocarbon selective catalytic reduction mechanism.

Removal of soot by non-thermal plasma oxidation as it flows through an unpacked reactor would require a relatively high energy input (joules per litre) achieved by either applying a considerable increase in applied energy or a considerable decrease in the exhaust gas flow to an impractical level. Trapping the soot so as to increase its residence time in the plasma reduces this energy requirement. In the plasma region, the soot becomes exposed to oxidative radicals such as O, OH, O<sub>3</sub> which then oxygenate the soot. The oxygenated soot has different activated and catalytic properties to unoxxygenated soot, which result in, for example, its oxidation at lower temperatures than would be observed using a purely thermal technique. The material for the selective filter for this purpose is primarily chosen for its ability to trap soot. Beads of alumina (CT530) provide a suitable material for this purpose, but may desirably be combined with a combustion catalyst material or a more soot-philic compound. Some improvement in the trapping effectiveness of the material may be provided by appropriate choice of the form in which the material is incorporated in a reactor, that is specifically whether it is incorporated in the form of sheets, wafers, meshes, frits, coils, spheres, pellets, extrudate, granules, fibres, foams or honeycomb monolith or as a coating on sheets, wafers, meshes, frits, coils, spheres, pellets, extrudates, granules, fibres or honeycomb monolith, foam, or membrane.

However, it is to be appreciated that using a packing material to trap soot in this way results in competition for the O-atoms and other oxidative species

which would otherwise be involved in the NO to NO<sub>2</sub> peroxy oxidation chain mechanism. The rates of reaction of O and other oxidative species with soot are faster than the hydrocarbon oxidation reaction so that conversion of NO  
5 to NO<sub>2</sub> is much less likely to occur.

This is then an example of how using a selective filter approach can significantly change the chemistry of a system. In this example, a dominant homogeneous gas  
10 phase reaction mechanism, plasma enhanced NO to NO<sub>2</sub> conversion is changed by the choice of a selective soot filter to promote an alternative heterogeneous soot oxidation mechanism using the same basic species found in the exhaust stream.

15

This has important implications for combined soot and NO<sub>x</sub> removal as this suggests that by removing the soot in a packed reactor you reduce the possibility for NO<sub>x</sub> reduction to nitrogen by a hydrocarbon selective  
20 catalytic reduction of NO<sub>2</sub>.

In accordance with the present invention, to achieve a combined soot and NO<sub>x</sub> removal this alteration in the chemistry taking place within the reactor as a  
25 consequence of trapping soot has to be taken into account. One approach is to use an NO selective catalyst such as a silver doped alumina catalyst, which functions by selectively adsorbing both the NO and also hydrocarbons and/or partially oxygenated hydrocarbons in  
30 the exhaust and promoting their reaction together to reduce NO directly to N<sub>2</sub>. The function of this silver doped alumina catalyst in this way is dependent upon the type of hydrocarbons and its performance may be improved

by activation of hydrocarbons in the exhaust gas stream by for example plasma activation, to form species such as partially oxygenated hydrocarbons, for example formaldehyde ( $\text{CH}_2\text{O}$ ). The presence of the non-thermal

5 plasma is important for this in that it is effective for the required activation of hydrocarbons at significantly lower temperatures than those required for thermal production of oxygenated hydrocarbons.

10 It will be apparent to those skilled in the art that this selective filter approach may be applied to other chemical processes, gases and exhaust streams.

The filter material may be selected for its ability  
15 to trap or adsorb a predetermined species in the destruction of toxic waste compounds for example those used in applications such as the micro-electronics and semi-conductor industries. Examples of these include species such as volatile organic compounds, halogen-  
20 containing compounds including perfluorocarbons, hydrofluorocarbons and Freons. Increasing the residence time of these species in the plasma by using a selective filter may result in an increase in the efficiency of their destruction.

25

In another example the selective filter material may be chosen for its ability to trap or adsorb a pre-determined species produced in the plasma to coat or modify the filter material in some way.

30

The filter material may be selected for its ability to trap or adsorb a predetermined species produced in the plasma to prevent a certain gas phase chemical reaction occurring. This could be to prevent a pollutant or toxin  
35 being formed or to act as an inhibitor for a certain



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isomer or molecule in a chemical process. As an example the filter material may be selected for its ability to trap or adsorb a predetermined polymer chain length or type from the gas phase in a plasma polymerisation process. The material could be selected to trap the polymer products required or to take out unwanted by-products to allow the desired product to be collected downstream.

Claims

1. A method of manufacturing a component for a non-thermal plasma reactor (300) for the treatment of gases, which method comprises assembling a bed of active material (320) in an enclosure having gas flow conduits (301,302) for directing gas to flow through or over the bed of active material (320), providing electrodes (303,310) adapted when electrically energised to generate non-thermal plasma in the gas, characterised in that at least a component of the active material is selected for its capability to adsorb or trap a predetermined chemical species in the gas flow thereby to increase the effective residence time of said species relative to the residence time of species in the gas flow which are not adsorbed or trapped and so modify the gas phase and/or surface chemistry of the treatment.

2. A method as claimed in claim 1 for the treatment of exhaust gases from an internal combustion engine, further characterised in that the said active material (320) or component thereof is selected for its capability to adsorb or trap a predetermined chemical species in the exhaust gas flow produced as a result of the combustion of fuel, and any modifier or additive therein, by the internal combustion engine.

3. A method as claimed in claim 1 or claim 2, further characterised in that the said active material (320) or component thereof is selected for its capability to adsorb or trap a predetermined chemical species in the gas flow produced by non-thermal plasma activation of constituents thereof.

4. A method as claimed in claim 2 or claim 3, further characterised in that the predetermined chemical species is from the group comprising nitrogen, oxygen, oxides of nitrogen such as NO, NO<sub>2</sub>, oxides of carbon such as CO, CO<sub>2</sub>, water, hydrocarbons including saturated, unsaturated, cyclic, branched and un-branched hydrocarbons, oxygenated hydrocarbons such as aldehydes, ketones, alcohols, acids ethers and esters, aromatic hydrocarbons and derivatives thereof including poly aromatic hydrocarbon compounds, oil fractions, fuel and partially burned fuel, air and air/fuel mixes, smoke, carbonaceous particulate including the soluble organic fraction and carbon, fine and ultrafine fraction, sulphur compounds including SO<sub>2</sub> and sulphates, organo-nitrogen species, acid gases, combustion modifiers/enhancers, additives such as urea, ammonia, cerium oxide (such as Eolys) and plasma activated species such as O, OH, O<sub>3</sub> activated hydrocarbons including partially oxygenated hydrocarbons/organic molecules and electronically and vibrationally excited state species.

5. A method as claimed in any of the preceding claims, further characterised in that the bed of active material (320) is provided in the form of sheets, wafers, meshes, frits, coils, spheres, pellets, extrudate, granules, fibres, foams or honeycomb monolith or as a coating on sheets, wafers, meshes, frits, coils, spheres, pellets, extrudates, granules, fibres or honeycomb monolith, foam, or membrane.

30

6. A method as claimed in any of the preceding claims, further characterised in that the active material (320) comprises dielectric or ferroelectric material.

7. A method as claimed in any of claims 1 to 5, further characterised in that the active material comprises polymeric material.

5 8. A method as claimed in any of claims 1 to 5, further characterised in that the active material comprises ceramic material.

9. A method as claimed in any of the preceding claims,  
10 further characterised in that dielectric barrier material (304) between the electrodes (303,310) establishes a dielectric barrier discharge type of reactor.

10. A method as claimed in any of claims 1 to 8, further  
15 characterised in that the electrodes are configured to provide a pulsed corona discharge type of reactor.

11. A method as claimed in any of claims 1 to 8, further characterised in that the electrodes are configured to  
20 provide a surface discharge type of reactor.

12. A method as claimed in any of the preceding claims, further characterised in that the electrodes (303,310) are configured to generate plasma in the gas as it flows  
25 over or through the bed of active material (320).

13. A non-thermal plasma reactor for the treatment of gases when made by a method as claimed in any of the preceding claims.

30

14. A non-thermal plasma reactor for the treatment of

gases, comprising a bed of active material (320) in an enclosure having gas flow conduits (301,302) for directing gas to flow through or over the bed of active material (320), electrodes (303,310) adapted when  
5 electrically energised to generate non-thermal plasma in the gas, characterised in that at least a component of the active material (320) is modified so as to adsorb or trap a predetermined chemical species in the gas flow to increase the effective residence time of the said species  
10 relative to the residence time of species in the gas flow which are not adsorbed or trapped and so modify the gas phase and/or surface chemistry of the treatment.

15 15. A non-thermal plasma reactor as claimed in claim 14, further characterised in that neither the plasma nor the said modified component is separately catalytic with respect to reactions of chemical species in the gas, but by virtue of the combined effect of the plasma and the adsorption or entrapment a catalytic effect on reactions  
20 is achieved.

16. A non-thermal plasma reactor as claimed in claim 14 or claim 15, further characterised in that the bed of active material (320) includes one or more catalysts from  
25 the group comprising alkali metal-exchanged zeolite Y or silver aluminate and other metal-exchanged or metal doped zeolite material including Cu/ZSM-5, Fe/ZSM-5, Co/ZSM-5, zeolite beta and hydrogen exchanged zeolites including H-ZSM-5, or the group comprising aluminas including alpha,  
30 gamma, chi and other crystalline phases, oxides of titanium, zirconium, cerium and vanadium, perovskites, spinels and mixtures of these materials, or metal doped inorganic oxides such as cobalt-doped aluminas.

35 17. A non-thermal plasma reactor as claimed in claim 16,

further characterised in that the bed of active material (320) includes a carbon combustion catalyst comprising one or more materials from the group comprising alkali metal oxide, or lanthanum oxide/alkali metal oxide/vanadium pentoxide, vanadates such as metavanadates and pyrovanadates

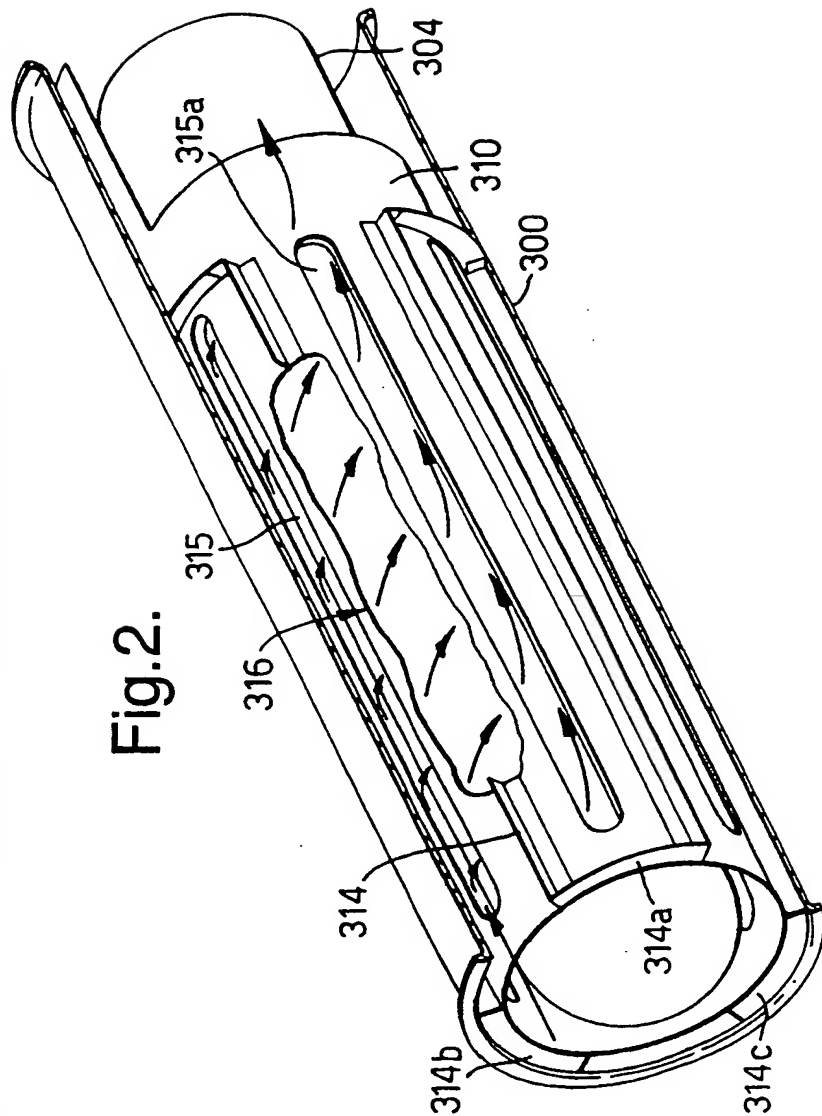
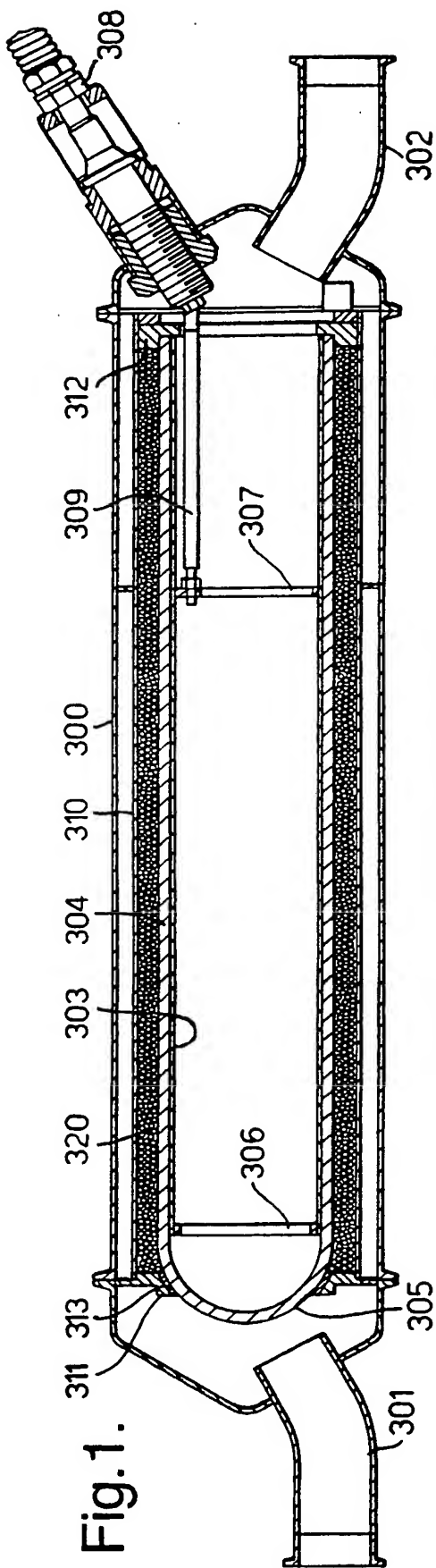
18. A non-thermal plasma reactor as claimed in claim 14 or claim 15 or claim 16 or claim 17, further characterised in that means are provided for controlling release of an adsorbed or trapped species.

19. A non-thermal plasma reactor as claimed in claim 18, further characterised in that the said means for controlling release of an adsorbed or trapped species comprises means for controlling the temperature of the modified component.

20. A non-thermal plasma reactor as claimed in any of claims 14 to 19, further characterised in that the said predetermined chemical species is carbonaceous soot, and desorption and/or decomposition of carbon functionalities formed therefrom and resultant production of carbon dioxide and carbon monoxide occurs at temperatures lower than the thermal oxidation temperature of carbonaceous soot.

21. A non-thermal plasma reactor as claimed in claim 20, further characterised in that the said resultant production of carbon dioxide and carbon monoxide occurs at temperatures lower than 250°C.

22. A non-thermal plasma reactor as claimed in claim 20, further characterised in that the said resultant production of carbon dioxide and carbon monoxide occurs at temperatures as low as 100°C.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03943

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/32 F01N3/08 F01N3/01 F01N3/027

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F01N B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 746 984 A (HOARD JOHN W) 5 May 1998 (1998-05-05)  column 5, line 53 -column 8, line 61; figures 1-4	1-6, 8-16, 18, 19
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) & JP 11 114351 A (SANDENSHA:KK;YAMAMOTO TOSHIKI; YOU SADAYOSHI), 27 April 1999 (1999-04-27) abstract	1, 13, 14, 18
A	US 5 715 677 A (VOGTLIN GEORGE E ET AL) 10 February 1998 (1998-02-10) abstract; figures	1, 14, 20-22
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

9 January 2001

Date of mailing of the international search report

15/01/2001

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 00/03943

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) &amp; JP 11 114359 A (AGENCY OF IND SCIENCE &amp; TECHNOL), 27 April 1999 (1999-04-27) abstract</p> <p>-----</p>	

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 00/03943

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5746984 A	05-05-1998	AU 3403397 A WO 9800221 A	21-01-1998 08-01-1998
JP 11114351 A	27-04-1999	NONE	
US 5715677 A	10-02-1998	NONE	
JP 11114359 A	27-04-1999	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)